Room Temperature Magnetoresistance and Cluster-Glass Behavior in the Tl$_{2-x}$Bi$_x$Mn$_2$O$_7$ ($0 \leq x \leq 0.5$) Pyrochlore Series

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In a novel Tl$_{2-x}$Bi$_x$Mn$_2$O$_7$ ($0 \leq x \leq 0.5$) pyrochlore series magnetoresistance (MR) dramatically increases with Bi substitution: A value of MR at 9 T of 10^4% is observed for Tl$_{1.8}$Bi$_{0.2}$Mn$_2$O$_7$ at 110 K; for Tl$_{1.9}$Bi$_{0.1}$Mn$_2$O$_7$ the room temperature MR (9 T) is 10^2%. Those values are unprecedented in pyrochlorelike manganese oxides, and open up the possibility of technological applications. A cluster-glass state develops, competing with ferromagnetism for $x \leq 0.1$ and preventing long range ferromagnetic ordering for $x \geq 0.2$. A new mechanism for MR at room temperature, associated with polaronic effects, is proposed. [S0031-9007(98)08158-7]

The broad classification of colossal magnetoresistance (CMR) materials includes those compounds in which magnetoresistance is associated with a ferromagnetic-to-paramagnetic phase transition [1], close to the Curie temperature (T_c). The prototypical CMR material is derived by hole doping of the parent perovskite LaMnO$_3$, for instance, in La$_{1-x}$A$_x$MnO$_3$ (A = alkali-earth). In conjunction with the double-exchange interaction, the existence of a strong electron-phonon coupling is also viewed as essential for a microscopic description of CMR in the manganite perovskites [2–4]. However, the observation of CMR in Tl$_2$Mn$_2$O$_7$ [5,6] shows that there can be causes other than double exchange for this phenomenon. Tl$_2$Mn$_2$O$_7$ crystallizes in the cubic pyrochlore-type structure, also constituted by vertex-sharing MnO$_6$ octahedra, with a characteristic Mn-O-Mn bond angle close to 133°. At variance with manganite perovskites, in Tl$_2$Mn$_2$O$_7$ the high-temperature state is metallic [5], there is no structural anomaly associated with the change in magnetotransport properties at $T_c = 142$ K, suggesting weak spin-lattice and charge-lattice correlations [7], and there is no Mn^{3+}-Mn^{4+} mixed-valence or Jahn-Teller distortions in the MnO$_6$ octahedra [8,9]. A superexchange-type interaction has been suggested to stabilize the ferromagnetic (FM) ordering of Mn spins [7], whereas the metallic conductivity comes from the overlap between Mn t_{2g}- and Tl 6s-block bands, resulting in a partial filling of the Tl 6s-block bands [10]. One possible explanation for the CMR effect in Tl$_2$Mn$_2$O$_7$ is strong scattering of conduction electrons by spin fluctuations (SF) associated with FM ordering on the Mn-O lattice [11]. This scenario implies the presence of two distinct electronic subsystems: itinerant (weakly magnetic), concerning the hybridization of Mn and Tl bands, and localized (strongly magnetic), involving the large local moment of Mn 3d electrons. The possibility of independently tuning the materials parameters rele-

vant in a SF model, through the substitution Sc for Tl in Tl$_{2-x}$Sc$_x$Mn$_2$O$_7$, has recently been shown [12]. In these pyrochlores, both resistivity and magnetoresistance are considerably enhanced over the undoped ($x = 0$) compound. It seems that scandium substitution mainly affects electronic conduction on the Tl-O sublattice while leaving magnetism essentially unchanged. Using this result to try novel substitutions which could improve both the physical properties of the parent Tl$_2$Mn$_2$O$_7$ compound and shed some light on the mechanism of magnetotransport in manganese pyrochlores was stimulating. Here we study the effect of substituting Bi for Tl in Tl$_{2-x}$Bi$_x$Mn$_2$O$_7$. Bismuth is trivalent like thallium, but it has a larger ionic radius (Tl^{3+}: 0.98 Å, Bi^{3+}: 1.17 Å) and, which is more important in describing the mixed Tl-Bi-Mn-O system, it has a 6s^2 electron lone pair able to participate in the chemical bonds to oxygens in the pyrochlore structure. Tl$_{2-x}$Bi$_x$Mn$_2$O$_7$ ($x = 0, 0.1, 0.2, 0.3, 0.4, 0.5$) pyrochlores were prepared under high-pressure conditions. The reaction was carried out in a piston-cylinder press, at a pressure of 20 kbar at 1000 °C for 1 h. The reaction products were characterized by x-ray diffraction: All of the reflections could be indexed in a cubic unit cell, the lattice parameter of which regularly increases with x, from **a** = 9.9052(5) Å for Tl$_2$Mn$_2$O$_7$, to **a** = 9.9514(7) Å for Tl$_{1.5}$Bi$_{0.5}$Mn$_2$O$_7$. This variation is consistent with the larger ionic radius for Bi^{3+} compared with that for Tl^{3+}. Neutron powder diffraction data, collected at D2B diffractometer (ILL-Grenoble) for $x = 0$ and $x = 0.2$ compounds and refined according to the conventional pyrochlore structure [13], space group Fd-3m, show that Mn-O distance slightly increases from 1.9016(9) Å for Tl$_2$Mn$_2$O$_7$ to 1.9029(9) Å for Tl$_{1.8}$Bi$_{0.2}$Mn$_2$O$_7$. Mn-O-Mn angles significantly increase from $x = 0$ [134.09(3)°] to $x = 0.2$ [134.41(3)°] materials. The dc and ac magnetic susceptibility were measured with a commercial

SQUID magnetometer on powdered samples; transport and magnetotransport measurements were performed by the conventional four probe technique, under magnetic fields up to 9 T in a physical properties measurement system (PPMS) from Quantum Design. The dc magnetic susceptibility vs temperature data (Fig. 1A) show a low-temperature saturation for $Tl_2Mn_2O_7$ characteristic of the long range FM ordering described earlier [5,6]. However, for $x > 0$ the presence of irreversibilities [differences between field-cooled (FC) and zero-field-cooled (ZFC) curves] even for $Tl_{1.9}Bi_{0.1}Mn_2O_7$ suggests the existence of antiferromagnetic (AFM) interactions competing with the net ferromagnetism exhibited by $Tl_2Mn_2O_7$. From the magnetization vs magnetic field curves, the saturation magnetic moments (M_s) are found to decrease from $2.65\mu_B/Mn$ for $Tl_2Mn_2O_7$ (close to that expected for Mn^{4+} of $3.0\mu_B$) to hardly $0.5\mu_B/Mn$ for $x = 0.5$, as indicated in Table I. This is in strong contrast with the observed behavior for the $Tl_{2-x}Sc_xMn_2O_7$ series [12], showing a relative insensitivity of M_s with x. On the

other hand, low-temperature neutron diffraction demonstrates the absence of long range magnetic ordering for $Tl_{1.8}Bi_{0.2}Mn_2O_7$, in contrast with the FM contribution to the neutron scattering on low-angle crystallographic reflections observed in $Tl_2Mn_2O_7$ below 110 K. In addition, specific heat measurements for $Tl_2Mn_2O_7$ show a sharp peak at 112 K related to FM ordering, in contrast with $Tl_{1.8}Bi_{0.2}Mn_2O_7$ for which no peak is observed in all of the temperature range. In the paramagnetic region, the inverse susceptibility $1/\chi$ vs T plot (Fig. 1B) shows a Curie-Weiss behavior only for temperatures higher than 220 K (i.e., $\approx 1.6T_c$ for $Tl_2Mn_2O_7$). The paramagnetic moment (p) reaches a maximum value for $x = 0.2$, p is within $(3.50-3.80)\mu_B/Mn$ (expected for spin-only Mn^{4+}, $3.80\mu_B$). For $T > T_c$, the presence of some magnetic correlations preclude the linear Curie-Weiss behavior; this regime could be described as a spin-polaron-like state, in the framework of a recent model for a low-density electron gas coupled to FM spin fluctuations [14]. The ac magnetic susceptibility measurements give evidence for a cluster-glass-like behavior which develops even for undoped $Tl_2Mn_2O_7$. For Bi substitutional levels $x \gtrsim 0.2$, the χ' decrease observed at low temperatures, strongly frequency dependent, is the signature for a cluster-glass behavior. In the χ'' susceptibility a broad maximum at 40 K for $x = 0$ and $x = 0.1$ compounds transforms into a sharp cusp at 38 K for $x = 0.2$, which is suppressed towards lower temperatures for increasing Bi-substitutional rates. This cusp corresponds to the crystallization of the cluster-glass state (T_{irr} in Table I). We believe that the spin-polaron-like state observed above T_c collapses at lower temperatures into the cluster-glass state below T_{irr}. It should be recalled that $A_2Mn_2O_7$ pyrochlores ($A =$ Sc, Y, Ho, Yb, and Lu) exhibit [15] clear FC-ZFC irreversibilities, and ac susceptibility results indicate the presence of both near-neighbor AFM and FM (second and third neighbor) short range correlations, in common with spin glasses. As the Bi-substitutional rate increases, the AFM interactions are favored by the further opening of the superexchange Mn-O-Mn angles (for instance, $134.40(3)°$ for $x = 0.2$ compared to $134.09°$ for $x = 0$) and the weakening (lengthening) of Mn-O bonds, giving rise to a completely disordered cluster-glass system at low temperatures for $x \gtrsim 0.2$.

Transport measurements were performed on "as-grown" pellets, directly sintered under the high-temperature/high pressure synthetic conditions. The transport properties show an extraordinary dependence of $\rho(T)$ with x (Fig. 2). $\rho(300\,K)$ increases by more than 6 orders of magnitude as x goes from 0 to 0.5 (see also Table I). This is associated mainly with the reduction in the concentration of Tl atoms, which is thought to be responsible for the large electronic conductivity of $Tl_2Mn_2O_7$, through the mixing of the voluminous Tl $6s$ orbitals with Mn $3d$ orbitals, in contrast with other insulating $A_2Mn_2O_7$ pyrochlores [15]. It is reasonable to
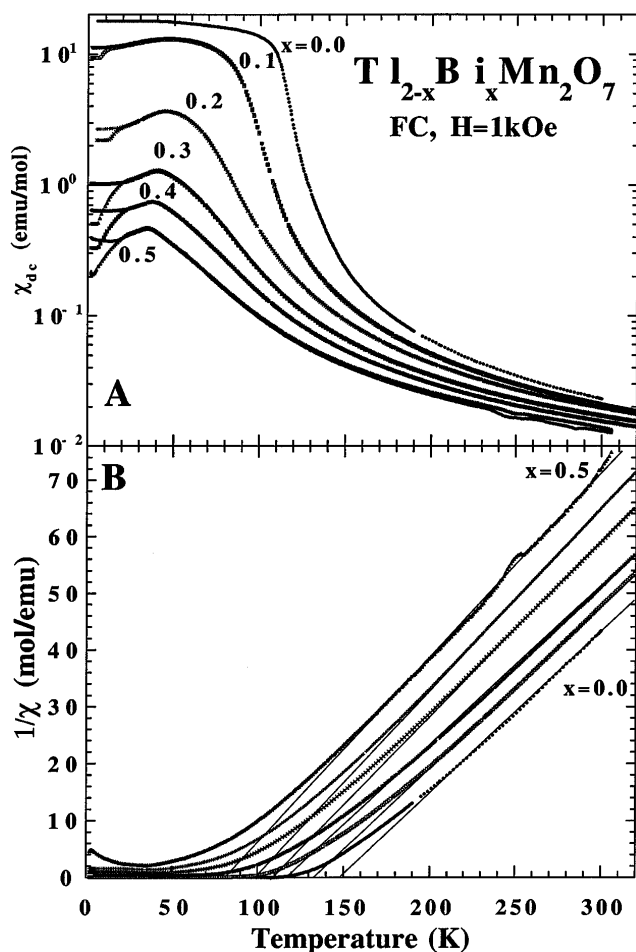

FIG. 1. (A) dc magnetic susceptibility as a function of temperature showing zero-field-cooled (lower) and field-cooled ($H = 0.1$ T, upper) curves; and (B) inverse susceptibility vs temperature. The straight lines are a guide to the eye.

TABLE I.   Magnetic and electrical parameters as a function of Bi concentration in $Tl_{2-x}Bi_xMn_2O_7$. Resistance data for RT. MR data are for RT and 9 T.

x	T_c (K)	T_{irr} (K)	M_s (μ_B)	p (μ_B)	ρ (Ω cm)	MR %	$E_{act}(0\ T)$ (meV)	$E_{act}(9\ T)$ (meV)
0.0	135	42	2.65	3.77	4.0×10^{-1}	10	$\cdots$	$\cdots$
0.1	95	40	1.85	3.76	1.0×10^{2}	100	94.9	68.1
0.2	$\cdots$	38	1.22	3.80	3.0×10^{3}	20	147	94.7
0.3	$\cdots$	36	0.71	3.61	1.0×10^{4}	6	$\cdots$	$\cdots$
0.4	$\cdots$	34	0.55	3.56	3.0×10^{5}	10	288	272
0.5	$\cdots$	32	0.52	3.50	7.0×10^{5}	$\cdots$	336	313

assume that Bi substitution introduces a strong-scattering $6s$ vacancy into the Tl-O network. The $6s^2$ electrons of Bi^{3+} are certainly not involved in the hybridization with Mn $3d$ orbitals, since they probably participate in strong covalent bonding to O' atoms, as happens in $Bi_2Ru_2O_7$ pyrochlore [16], and, therefore, Bi is not capable of contributing states at the Fermi level. From preliminary far-infrared reflectivity measurements [17] the number of carriers (electrons) at 77 K has been estimated to decrease
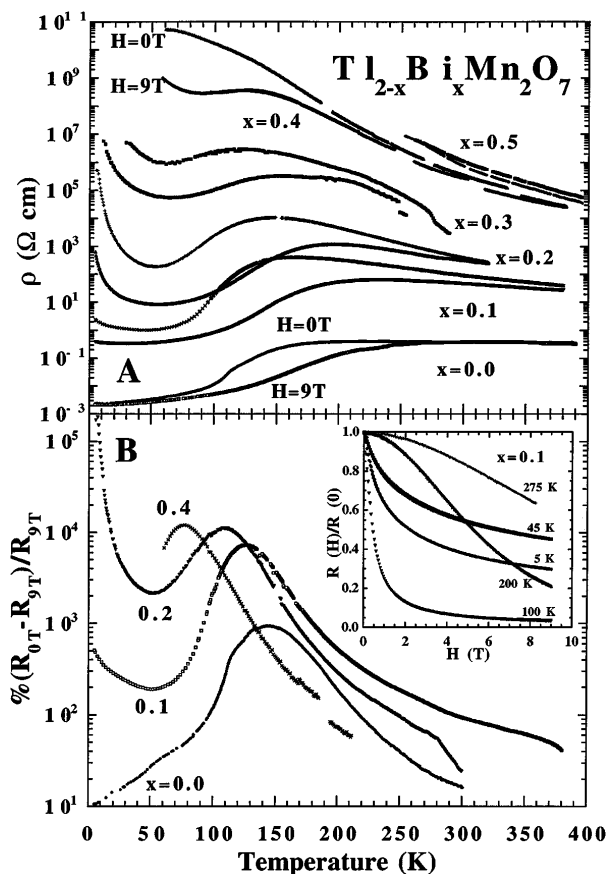

FIG. 2.   (A) Resistivity vs temperature plots at $H = 0$ (upper) and 9 T (lower) curves; and (B) temperature variation of the magnetoresistance at $H = 9$ T, defined as MR(9 T) = $100x[R(0) - R(9\ T)]/R(9\ T)$ for $Tl_{2-x}Bi_xMn_2O_7$. The inset shows the magnetic field dependence for $Tl_{1.9}Bi_{0.1}Mn_2O_7$ at four selected temperatures.

by a factor of 2 from $Tl_2Mn_2O_7$ to the $x = 0.1$ compound. The evolution of $\rho(T)$ is also strongly x dependent (see Fig. 2A): For $x \geq 0.1$ a semiconductinglike behavior is observed at high temperatures, leading to a maximum in resistivity, followed by a minimum at lower temperatures, and, for $x \geq 0.2$, a new increase in ρ below 50 K. This localization at low temperature could be related to the freezing temperature (T_{irr}) of the cluster-glass state for doping levels $x \geq 0.2$. Regarding the changes in $\rho(T)$ under a magnetic field we define MR(9 T) = $100x[R(0) - R(9\ T)]/R(9\ T)$.   The   evolution   of MR(9 T) with x is spectacular: As shown in Fig. 2B, MR(9 T) increases from $9.5 \times 10^2\%$ ($x = 0$, $T = 145$ K) to $7.0 \times 10^3\%$ for $x = 0.1$ at 125 K. For $Tl_{1.8}Bi_{0.2}Mn_2O_7$ this maximum is shifted to 110 K and MR(9 T) is of the order of $10^4\%$, and, below 50 K MR(9 T) dramatically increases, taking values higher than $10^5\%$ at 10 K. This is related to the huge increase in ρ for doping levels $x \geq 0.2$ when the external field is zero and the cluster-glass state is established: Through the application of a strong magnetic field the magnetic clusters become oriented and the size of the FM domains increases, dramatically reducing the spin fluctuation scattering and, therefore, the electrical resistance. The occurrence of CMR coupled to a spin-glass state had been observed in perovskite-related compounds, such as $(TbLa)_{2/3}Ca_{1/3}MnO_3$ [18] or $RNi_{0.3}Co_{0.7}O_3$ [19], but this is the first report of CMR associated with a cluster-glass state in pyrochlore-type compounds. The inset in Fig. 2B shows the magnetic field dependence of MR [given as $R(H)/R(0)$] for $Tl_{1.9}Bi_{0.1}Mn_2O_7$ at some selected temperatures. It is remarkable that most of the magnetoresistant effect at $T = 100$ K, close to T_c, is obtained at low field ($H < 2$ T), with a slope higher than -2 T^{-1}. This feature is in contrast with that observed in manganese perovskites, i.e., $La_{0.7}Ca_{0.3}MnO_3$, where roughly 50% of the MR effect is obtained at low field, whereas the remaining 50% is a high-field effect. This result suggests that in Bi-substituted pyrochlores the grains are fully magnetized and the grain boundary is extremely small compared with the grain volume. Moreover, the most remarkable feature of the $Tl_{2-x}Bi_xMn_2O_7$ system lies in the room temperature (RT) behavior. As indicated in Table I, RT MR(9 T) value for $Tl_2Mn_2O_7$ is 10%,
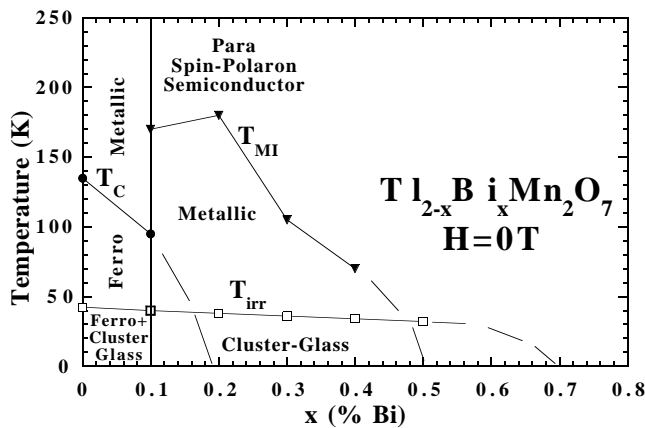
FIG. 3. Phase diagram for the $Tl_{2-x}Bi_xMn_2O_7$ system. T_c: ferromagnetic Curie temperature; T_{irr}: cluster-glass freezing temperature from the magnetic susceptibility irreversibility; T_{MI}: metal-to-insulator transition temperature.

enhanced up to a maximum of $10^2\%$ for $Tl_{1.9}Bi_{0.1}Mn_2O_7$. This is comparable to the best results obtained for perovskite manganites, with large cations at the A positions, showing MR in the $10^2\%$ range [20]. At present, MR in pyrochlores was described only to occur below 200 K: The possibility of achievement of large MR at RT was supposed to be associated with the increase of T_c, perhaps with the use of magnetic ions with larger exchange energies instead of Mn. The present results show that Bi substitution may enhance RT and low-field MR up to levels which makes it possible for one to propose these materials as candidates for technical applications. We propose that this effect is related to the spin-polaron conductivity, which is mainly responsible for the transport in that temperature regime. The resistivity at $T > \Theta_W$ can be described by an Arrhenius law with activation energies E_{act} ranging from 95 meV ($x = 0.1$) to 336 meV ($x = 0.5$) (see Table I). E_{act} is strongly dependent on the external magnetic field, giving a maximum reduction at 9 T of 36% for the $x = 0.2$ pyrochlore. The observed reduction in resistivity under an applied field is explained by both the increase in the concentration of spin polarons and their spin alignment parallel to the magnetic field. The strong decrease of the activation energy, of about $-3.5\%T^{-1}$, suggests a purely magnetic polaron, localized by a polarization cloud (spin-bag). Preliminary data on small-angle neutron scattering indicate a correlated size for magnetic polarons at about 10–15 Å near RT [21]. This polaron size is close to that observed in magnetoresistant perovskites [3]. All of the available information is presented in the phase diagram shown in Fig. 3. For low Bi-substitutional levels ($x \leq 0.1$) the system is metallic and orders ferromagnetically with a reentrant spin-glass behavior at low temperature. For higher Bi contents,

$x \gtrsim 0.2$, the system is magnetically frustrated, showing a cluster-glass-like behavior below characteristic freezing temperatures (T_{irr}) close to 40 K, and metal-to-insulator transitions at T_{MI} temperatures which strongly decrease as x increases. We have shown that moderate pressure synthesis techniques can be used to prepare a Bi-substituted series of pyrochlores based on $Tl_2Mn_2O_7$, in which magnetoresistance is hugely enhanced. For the first time we show the occurrence of CMR coupled to a cluster-glass state in a pyrochlore system: It is thought that the application of an external field increases the size of the ferromagnetic domains, hence, diminishing the spin fluctuation scattering in the sample. At variance with mixed-valence manganese perovskites, in which RT MR is achieved by pushing up T_c, in the $Tl_{2-x}Bi_xMn_2O_7$ series we show that the occurrence of localized 10–15 Å magnetic polarons at $T > \Theta_W$ accounts for the large MR (up to 10^2 for an $x = 0.1$ compound) observed at room temperature, well above T_c. Those MR values are unprecedented in pyrochlorelike manganese oxides, and open up the possibility of technological application for these materials.

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